



A natural sorbent, *Luffa cylindrica* for the removal of a model basic dye

Aylin Altınışık, Emel Gür, Yoldaş Seki*

Dokuz Eylül University, Faculty of Arts and Sciences, Department of Chemistry, Tınaztepe Campus, Buca İzmir, Turkey

ARTICLE INFO

Article history:

Received 21 January 2010

Received in revised form 3 March 2010

Accepted 12 March 2010

Available online 19 March 2010

Keywords:

Dye removal

Luffa cylindrica

Sorption kinetics

Thermodynamic aspects

ABSTRACT

In this work, application of *Luffa cylindrica* in malachite green (MG) removal from aqueous solution was studied in a batch system. The effect of contact time, pH and temperature on removal of malachite green was also investigated. By the time pH was increased from 3 to 5, the amount of sorbed malachite green also increased. Beyond the pH value of 5, the amount of sorbed malachite green remains constant. The fits of equilibrium sorption data to Langmuir, Freundlich and Dubinin–Radushkevich equations were investigated. Langmuir isotherm exhibited best fit with the experimental data. Monolayer sorption capacity increased with the increasing of temperature. Sorption kinetic was evaluated by pseudo-first-order, pseudo-second-order, Elovich rate equations and intraparticle diffusion models. It was inferred that sorption follows pseudo-second-order kinetic model. Thermodynamic parameters for sorption process were also found out. Spontaneous and endothermic nature of sorption was obtained due to negative value of free energy (ΔG°) and positive value of enthalpy (ΔH°) changes. FTIR analyses were also conducted to confirm the sorption of malachite green onto *L. cylindrica*.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Dyes are widely used in industries such as textiles, leather, paper, plastics, etc. to color their final products. Wastewater containing even a small amount of dyes can severely affect the aquatic life due to the reduction of light penetration and their toxicity [1]. Many dyes and color effluents are toxic and have carcinogenic and mutagenic effects that influence environment and also human. Dye removal from wastewater effluent is a major environmental problem because of the difficulty of treating such streams by conventional physical, chemical, physico-chemical and biological treatment methods. Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye-containing effluents [2,3]. Adsorption process is one of the most effective and economically feasible methods for the removal of dyes from aqueous solutions.

Various kind of adsorbents which have been reported such as activated carbon [4], sugarcane dust, algae, red algae [5], macro fungus [6], green alga [7], lichen [8], saw dust, bottom ash, fly ash, de-oiled soya, maize cob, peat, iron humate, mixed sorbents, microbial biomass, activated slag, waste product from agriculture, bentonite, magnetic nanoparticle, coal were used for the removal

of color and trace elements from wastewater [9]. Activated carbon which has high adsorption capacity for organic matters remains an expensive material.

Malachite green (MG) is most commonly used for the dyeing of cotton, silk, paper, leather and also in manufacturing of paints and printing inks. It is also extensively used as a bactericide, fungicide and parasiticide in aquaculture industries worldwide. Malachite green is highly toxic to mammalian cells and causes kidney tumors in mice and reproductive problems in rabbit and fish [10].

Adsorption of malachite green on activated carbon has been reported elsewhere [11,12]. Also a number of non-conventional sorbents has been studied in the literature for their capacity to remove malachite green from aqueous solutions, such as *Prosopis cineraria* [13], hen feathers [14], modified rice straw [15] and carbon based adsorbents [16].

Luffa cylindrica is produced abundantly in many developing countries within the tropical and subtropical zones, primarily for use in bathing and washing. *L. cylindrica*, a natural material consisting of cellulose and lignin (1.4:2.9% of sponge dry weight) [17], belongs to Cucurbitaceae family. *L. cylindrica* has fruits possessing a netting-like fibrous vascular system (*Luffa* sponges). The struts of this natural sponge are characterized by microcellular architecture with continuous hollow micro channels (macro pores with diameter of 10–20 μm) which form vascular bundles and yield a multimodal hierarchical pore system. It is used as a vegetable either prepared like squash or eaten raw like cucumbers [18]. Recently, *Luffa* sponges have been applied as cell carriers in bioreactors [19], scaffolds for tissue engineering [20] and for the development of biofiber-reinforced composites [21].

* Corresponding author. Tel.: +90 232 4128705; fax: +90 232 4534188.
E-mail address: yoldas.seki@deu.edu.tr (Y. Seki).

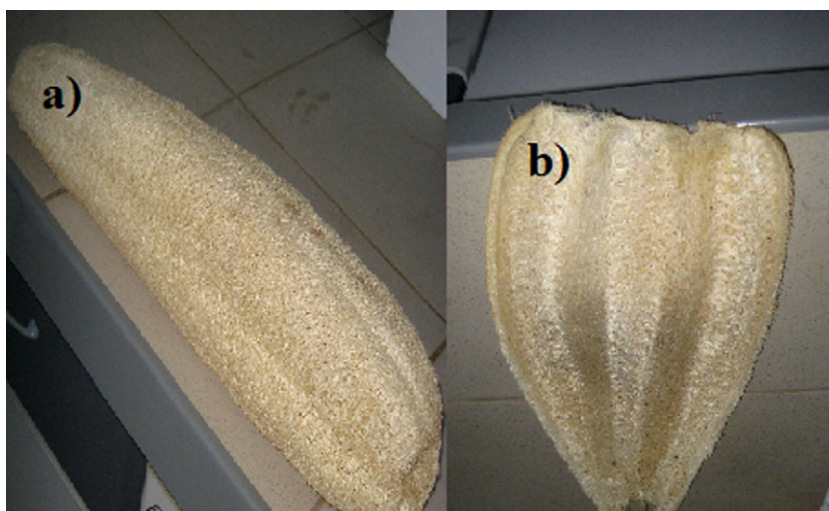


Fig. 1. a) Sponge guard and b) outer mat core.

In this study *L. cylindrica* fibers have been used for malachite green removal from aqueous solution at different temperature and pH values. Thermodynamic and kinetic parameters have also been investigated.

2. Materials and methods

Malachite green used in this study was purchased from Carlo Erba. Its chemical formula and molecular weight are $C_{23}H_{25}ClN_2$ and $364.90 \text{ g mol}^{-1}$, respectively. HCl was obtained from Riedel-de Haen. *L. cylindrica* which was shown in Fig. 1 was purchased from a local specialty shop in İzmir; Turkey. To separate the inner fiber core from outer mat core, the as-received sponge-gourd was cut carefully. Only the outer mat core of Luffa was utilized in this study. Luffa fibers were dipped in 2% NaOH solution for about 60 min. NaOH was purchased from Riedel-de Haen. Treated Luffa fibers were washed with distilled water until a neutral pH was reached and then dried at 60°C for 24 h. Thereafter, they were cut to 2–3 mm.

Batch adsorption technique was performed by adding 0.05 g alkalized *L. cylindrica* (AL) into conical flasks containing 20 mL of different initial concentrations ($20\text{--}100 \text{ mg L}^{-1}$) of aqueous solution of malachite green at 15, 25 and 35°C temperatures. The flasks were subjected to agitation in GFL 1086 isothermal water-bath shaker at 200 rpm at different temperatures for 5 h to reach equilibrium state. Supernatant liquid was taken from the solutions and the concentrations were analyzed by using UV/Vis spectrophotometer (Shimadzu, Model UV 1601) at 618 nm.

The amount of uptake of malachite green by the AL in the equilibrium, q_e (mg g^{-1}) was estimated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where V is the volume of solution and m is the mass of sorbent used in this study. C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentration of malachite green, respectively.

The effect of pH on adsorption of MG onto AL has been monitored at different pH values (3–10) (Inolab WTW). Experimental conditions such as, initial dye concentration, shaking time, temperature and the amount of adsorbent were fixed at 20 ppm, 200 min^{-1} , 308 K, 0.05 g of AL fibers. The pH values of initial solutions were adjusted by adding a few drops of diluted 0.1 N NaOH or 0.1 N HCl.

For kinetic studies, 0.05 g of AL was contacted with 20 mg L^{-1} malachite green solutions (20 mL) using a water-bath shaker at 200 rpm at different temperatures. At predetermined time

intervals, the amount of uptake malachite green was evaluated spectrophotometrically.

Infrared spectral analyses of AL and malachite green sorbed AL (MGAL) were conducted by using Perkin Elmer FTIR spectrophotometer (Spectrum BX-II). KBr pellets were prepared for the measurements.

3. Results and discussion

3.1. Sorption kinetics

The effect of contact time on sorption of malachite green onto AL at different temperatures was shown in Fig. 2. As can be seen from Fig. 2, the amount of sorbed MG is rapid at early stages and becomes slow with increasing of time and gradually approaches equilibrium state. When Fig. 2 was taken into account, 5 h may be considered as sufficient time to reach equilibrium state.

To gain a better understanding adsorption kinetics and rate-limiting step, several kinetic models were used. These kinetic models are Lagergren-first-order model, pseudo-second-order kinetic model, Elovich's model and Intraparticle diffusion model.

Lagergren equation was used to investigate the suitability of pseudo-first-order kinetic model and obtain rate constants [22].

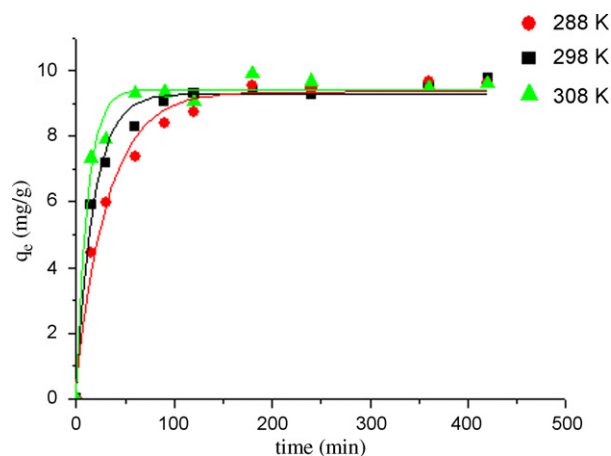


Fig. 2. Effect of contact time on sorption of malachite green onto *Luffa cylindrica* ($C_0 = 20 \text{ mg L}^{-1}$).

Table 1
Kinetic parameters for the sorption of MG onto *L. cylindrica*.

	288 K	298 K	308 K
$q_{e, \text{exp}}$ (mg g ⁻¹)	9.76	9.68	9.92
Lagergren-first-order			
k_1 (min ⁻¹)	0.053	0.053	0.018
q_e (mg g ⁻¹)	16.71	37.33	2.01
R^2	0.935	0.775	0.532
Pseudo-second-order equation			
k_2 (g mg ⁻¹ min ⁻¹)	0.004	0.009	0.013
q_e (mg g ⁻¹)	10.02	10.13	10.67
$t_{1/2}$ (min)	24.95	10.97	7.21
$h_{0,2}$ (mg g ⁻¹ min ⁻¹)	0.40	0.92	1.48
R^2	0.999	0.998	0.996
The Elovich equation			
α	2.45	52.48	2.11
β	1.42	1.01	2.13
R^2	0.890	0.954	0.800
Intraparticle diffusion equation			
k_{int} [mg/(g min ^{1/2})]	0.37	0.53	0.25
R^2	0.878	0.953	0.829

This equation can be written as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the amount of MG sorbed at equilibrium and at any time t , respectively, and k_1 (min⁻¹) is the rate constant for Lagergren-first-order sorption. The straight-line plots of $\log(q_e - q_t)$ against t of Eq. (2) were made at different temperatures (288, 298 and 308 K). The parameters were summarized in Table 1. From the linear correlation coefficients (R^2), it is seen that Lagergren equation does not represent a good fit with the experimental data.

Pseudo-second-order kinetic model [23] can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant for the pseudo-second-order kinetic model. The q_e and k_2 values were estimated from the slope ($1/q_e$) and intercept ($1/k_2 q_e^2$) of linear plot of t/q_t versus t at different temperatures. The calculated parameters were presented in Table 1. The linear correlation coefficients were obtained to be 0.999, 0.998, and 0.996 for 288, 298 and 308 K, respectively. This implies the validity of pseudo-second-order kinetics for both temperatures. Also, as shown in Table 1, due to fact that the calculated amounts of sorbed MG at equilibrium were close to experimental values, it can be said that sorption of MG onto AL follows the pseudo-second-order kinetic model.

The initial rate of sorption was estimated from pseudo-second-order kinetic model from the below equation:

$$h_{0,2} = k_2 q_e^2 \quad (4)$$

The results were presented in Table 1. The highest initial rate of sorption was obtained at highest temperature (308 K) in the studied temperature range.

The half-sorption time, $t_{1/2}$ known as the time required for the sorption to take up half as much AL as its equilibrium value. This time is often used as a measure of the adsorption rate [24].

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (5)$$

The half-sorption time values at different temperatures were presented in Table 1. The lowest half-sorption time was obtained at highest studied temperature (308 K) in this study.

The Elovich rate equation was analyzed for applicability of sorption data. The Elovich equation can be given by the below

expression

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (6)$$

where β (g mg⁻¹) is related to the extent of surface coverage and activation energy for chemisorption and α (mg g⁻¹ min⁻¹) is the initial sorption rate. R^2 values for the Elovich equation were lower than those for pseudo-second-model. It is known that the Elovich equation is useful in describing sorption on highly heterogeneous sorbents [25].

When the diffusion (internal surface and pore diffusion) of MG molecules inside the adsorbent is the rate-limiting step, then adsorption data can be given by the following equation [25–27]:

$$q_t = k_i t^{1/2} \quad (7)$$

where k_i [mg/(g min^{1/2})] is the intraparticle diffusion rate constant. The k_i values are found from the slopes of q_t versus $t^{1/2}$ plots, as presented in Fig. 3.

If the intraparticle diffusion is involved in the adsorption processes, then the plot of the square root of time versus the amount of sorbed (q_t) must give a straight line with a slope that equals k_i and an intercept equal to zero [28]. Namely, the intraparticle diffusion would be controlling step if this line passed through the origin. As can be seen from Table 1, the intraparticle diffusion did not control the adsorption process since the linear correlation coefficient values of model for the plots were in the range 0.829–0.953. Moreover, since the plots do not pass through the origin, this indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption [25,27].

3.2. The effect of initial pH of solution

pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites [24]. The effect of initial solution pH on sorption of MG onto AL was shown in Fig. 4. As can be seen in Fig. 4, when pH was increased from 3 to 5, the adsorption capacity increased significantly. However when pH was increased from 5 to 10, adsorption reached equilibrium. Furthermore pH value of 5 is the own pH value of MG solution. Consequently acidic medium affected the adsorption negatively. At low pH values, protonation of malachite green ($pK_a = 10.3$) occurs. However, with increasing of pH, malachite green becomes more

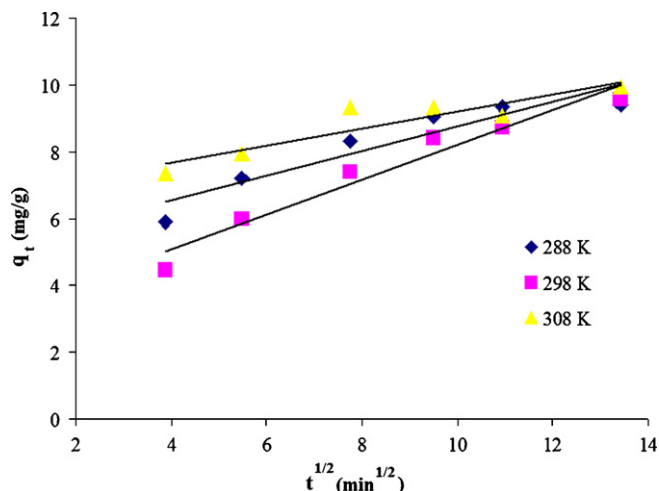


Fig. 3. Intraparticle diffusion plots at different temperatures.

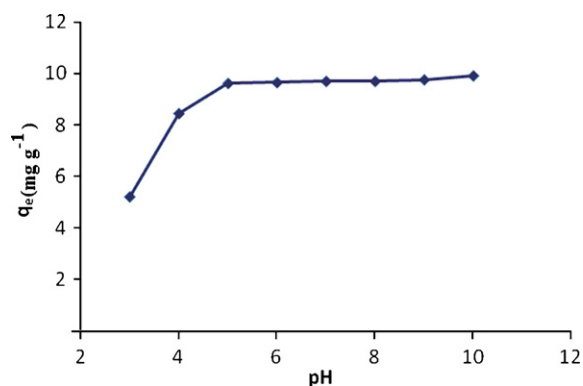


Fig. 4. The effect of initial pH of solution on adsorption of MG onto *Luffa cylindrica* fibers. 20 ppm MG solution, 308 K, 0.05 g adsorbent, 200 min⁻¹.

deprotonated. It is probable that low sorption of malachite green at low pH values indicates possibility of formation of positive charge on the sorbent, thereby preventing the sorption of malachite green onto itself. In addition to this, because of the electrostatic repulsion among the sorbed positively charged dye cations, malachite green sorption might have decreased at low pH values. Moreover decreasing of sorption below the pH value of 5, may be also attributed to a competition between H⁺ ions and protonated dye ions for the sorption sites. Similar results were also reported by other studies for MG sorption onto various sorbents [14,28,29].

3.3. Adsorption isotherms

The adsorption isotherm is the most important information which indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those Langmuir, Freundlich, and Dubinin–Radushkevich were used to describe the equilibrium characteristics of adsorption. The linear form of Langmuir isotherm is expressed as

$$C_e/q_e = 1/(Lq_m) + (C_e/q_m) \quad (8)$$

where q_e is the amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg g⁻¹) and C_e is the equilibrium concentration of dye in solution (mg L⁻¹). The constant q_m is the monolayer sorption capacity (mg g⁻¹) and L is related with the energy of the adsorption (L mg⁻¹). Plots of C_e/q_e versus C_e (Fig. 5) yield a straight

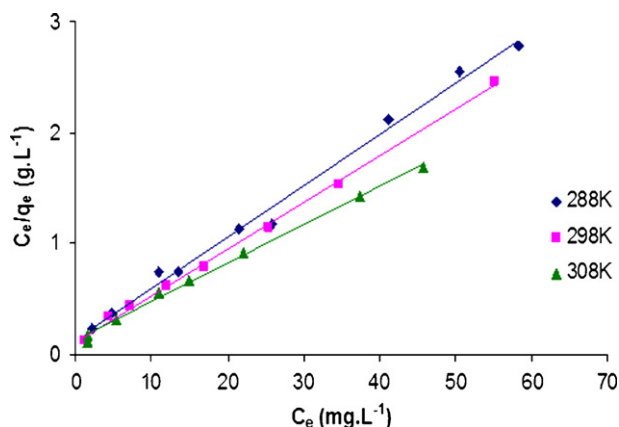


Fig. 5. Linearized Langmuir isotherms at different temperature.

Table 2

Langmuir, Freundlich, and Dubinin–Radushkevich model constants and correlation coefficients for sorption of MG onto Luffa.

Langmuir isotherm				
Temperature (K)	L (Lmg ⁻¹)	q_m (mg g ⁻¹)	R_L	R^2
288	0.33	21.6	0.0296	0.993
298	0.41	23.8	0.0237	0.998
308	0.28	29.4	0.0349	0.996
Freundlich isotherm				
Temperature (K)	n_f	K_f (mg g ⁻¹)	R^2	
288	4.1	8.4	0.867	
298	2.4	9.5	0.937	
308	3.8	10.4	0.891	
Dubinin–Radushkevich Isotherm				
Temperature (K)	β (mol ² J ⁻²)	X_m (mol g ⁻¹)	E (kJ mol ⁻¹)	R^2
288	2.0×10^{-9}	1.446×10^{-4}	15.8	0.924
298	2.0×10^{-9}	1.12×10^{-4}	15.8	0.946
308	2.0×10^{-9}	2.070×10^{-4}	15.8	0.899

line with slope $1/q_m$ and intercept $1/q_m L$. Table 2 lists the maximum adsorption capacity q_m values for malachite green sorption onto the AL at different temperatures.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L given by [30,31]

$$R_L = \frac{1}{1 + L \times C_0} \quad (9)$$

where L is the Langmuir constant and C_0 is the highest initial dye concentration (mg L⁻¹). According to the value of R_L (Table 3) the type of sorption may be interpreted as follows: values of R_L calculated at 288, 298 and 308 K are in range between 0 and 1 which indicate that the adsorption is favorable at operation conditions studied.

The Freundlich isotherm [32] is an empirical equation based upon a heterogeneous surface. A linear form of the Freundlich expression can be presented as below

$$\log q_e = \log K_f + n_f \log C_e \quad (10)$$

A plot of $\log q_e$ versus $\log C_e$ enables to determine the constant K_f and n_f . K_f represents the quantity of dye adsorbed onto adsorbent for an equilibrium concentration. The slope n_f , ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. These values together with the correlation coefficients are summarized in Table 2. Based upon the correlation coefficients (R^2) shown in Table 2, it can be said that the adsorption data can be described by Langmuir equation. Also, the fit of the experimental data to Langmuir equation is better than that of Freundlich equation.

In order to calculate the mean free energy value of sorption, Dubinin–Radushkevich (DR) isotherm has also been applied for the sorption of MG onto AL. The DR equation can be defined by the following equation [33,34]

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad (11)$$

Table 3

R_L values of Langmuir isotherm.

Value of R_L	Type of adsorption
$R_L > 1.0$	Unfavorable
$R_L = 1.0$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

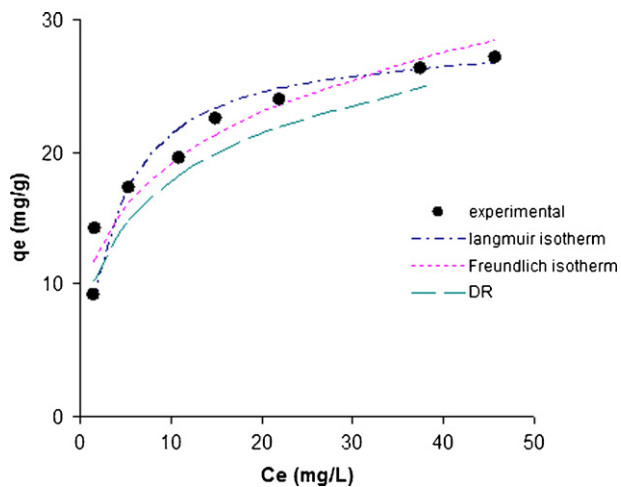


Fig. 6. The suitability equilibrium data in Freundlich, Langmuir and DR isotherms at 308 K.

where β is the constant related to sorption energy ($\text{mol}^2 \text{J}^{-2}$), X_m is the Dubinin–Radushkevich monolayer capacity (mol g^{-1}), q_e is the amount of dye sorbed per unit weight of AL (mg g^{-1}), ε is the Polanyi potential which can be obtained as follows:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

where C_e is the equilibrium concentration of dye (mol L^{-1}), R gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T the temperature (K). By plotting $\ln q_e$ versus ε^2 , it is possible to determine the value of β from the slope and the value of X_m from the intercept, which is $\ln X_m$.

The mean free energy E (kJ mol^{-1}) of sorption can be estimated by using β values as expressed in the following equation [35–37].

$$E = \frac{1}{(2\beta)^{-1/2}} \quad (13)$$

The parameters obtained using above equations were summarized in Table 2. Adsorption capacity (X_m) values increased with the increasing of temperature from 288 to 308 K. Since E values are in the range 8–16 kJ mol^{-1} the adsorption type can be considered as ion exchange. However, we must take lower compatibility of sorption data to DR isotherm into consideration.

Fig. 6 shows the fitted equilibrium data in Freundlich, Langmuir and DR isotherms. It can be seen in Fig. 6 that Langmuir isotherm fits the data better than Freundlich and DR isotherms. This is also confirmed by the high value of R^2 in case of Langmuir (0.996) compared to Freundlich (0.891) and DR (0.899) and this indicates that the adsorption of MG on AL takes place as monolayer sorption on a surface that is homogenous in sorption affinity.

AL sorbent used in this work had a relatively large sorption capacity (29.3 mg g^{-1}) compared to some other sorbents reported in the literature, such as bentonite clay [38] (7.72 mg g^{-1} , $T = 35^\circ \text{C}$), *Arundo donax* root carbon [39] (8.7 mg g^{-1} , $T = 30^\circ \text{C}$) and activated charcoal [40] (0.179 mg g^{-1} , $T = 30^\circ \text{C}$). This indicates that *L. cylindrica* is effective to remove MG from aqueous solutions.

3.4. Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were estimated for MG sorption onto AL. ΔG° values at different temperatures were calculated from the following equations

$$\Delta G^\circ = -RT \ln K_d \quad (14)$$

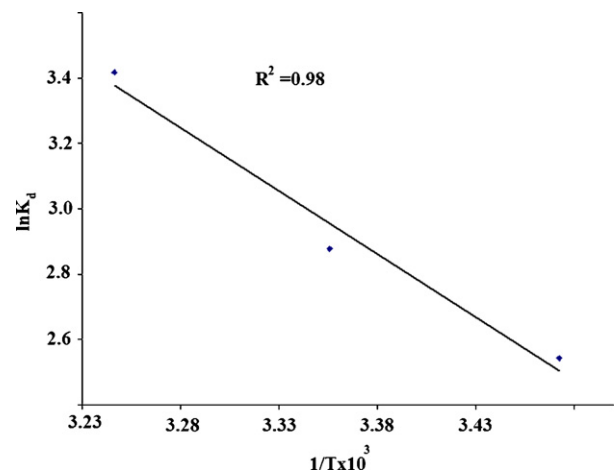


Fig. 7. Plot of $\ln K_d$ versus $1/T$.

$$K_d = \frac{q_e}{C_e} \quad (15)$$

where q_e is the amount of MG (mg) sorbed by AL per L of solution at equilibrium, C_e is the equilibrium concentration (mg L^{-1}) of MG in solution, K_d is the distribution coefficient for the sorption.

The average standard enthalpy change (ΔH°) is obtained from Van't Hoff equation:

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (16)$$

where T is the absolute temperature, R is gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). From the slope and the intercept of the plot of $\ln K_d$ versus $1/T$, as presented in Fig. 7, ΔH° and ΔS° values were calculated. The calculated parameters by using above equations were presented in Table 4.

As can be seen in Table 4, ΔG° values were obtained to be -6.1 , -7.1 and -8.7 kJ mol^{-1} for 288, 298 and 308 K, respectively. Negative value of Gibbs free energy values shows the spontaneous nature of MG sorption on AL. The positive value of enthalpy change (ΔH°) indicates endothermic nature of sorption. Endothermic nature of process is an expected result because of the fact that Langmuir monolayer capacity increases with increasing temperature. The positive value of ΔS° demonstrates some structural changes at the solid–liquid interface. Besides, the positive ΔS° favors ion exchange and stability of sorption [21].

The absolute magnitude of ΔG° may give an idea about the type of adsorption. Chemisorption has an energy range 80–400 kJ per unit mole, physical sorption has a range 0 to -20 kJ per unit mole [41]. Since ΔG° values obtained in this study are in the range 0 to -20 kJ mol^{-1} , sorption of MG onto AL can be considered as physisorption process.

3.5. FTIR results

FTIR spectra of alkalized Luffa (AL) and malachite green sorbed alkalized Luffa (MGAL) were presented in Fig. 8. A broad band at about 3418 cm^{-1} could be assigned to OH^- stretching vibrations of AL. After adsorption of malachite green, this band shifted to 3424 cm^{-1} and became sharper. The bands at about 2915 cm^{-1}

Table 4
Thermodynamic parameters for the sorption of MG onto *L. cylindrica*.

ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})	ΔG° (kJ mol^{-1})		
		288 K	298 K	308 K
32.1	132.2	-6.1	-7.1	-8.7

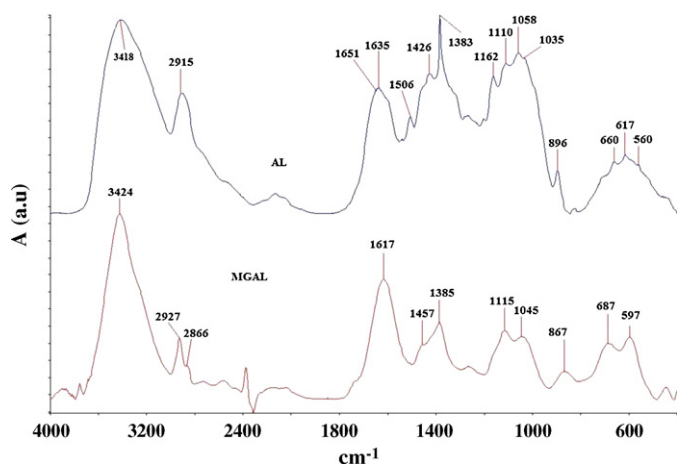


Fig. 8. FTIR spectra of AL and MGAL.

correspond to CH_2 and CH_3 stretching vibrations. As can be seen from the spectrum of MGAL, this band split in two at 2927 and 2866 cm^{-1} . The band at 2866 cm^{-1} seems to be a shoulder. The band H–O–H bending of adsorbed water which was seen at 1635 cm^{-1} in the spectrum of AL decreased to 1617 cm^{-1} and became sharper after MG adsorption. Benzene ring stretching (lignin) in the spectrum of AL which was detected at 1506 cm^{-1} disappeared after MG adsorption. CH_2 and CH_3 bending was located at 1426 cm^{-1} . C–H bending was seen at 1383 cm^{-1} . However, the intensities of these bands became weaker after MG adsorption. C–O–C antisymmetric bridge in stretching in cellulose and hemicelluloses was located at 1162 cm^{-1} . This band cannot be seen clearly after MG adsorption. C–OR stretching (cellulose) was observed at 1058 cm^{-1} . β -Glucosidic linkage was recorded at 896 cm^{-1} and shifted to 867 cm^{-1} as a consequence of MG adsorption. As a result, FTIR analysis revealed some changes which occur on functional groups of AL.

4. Conclusion

With this study, it has been shown that *L. cylindrica* can be used as efficient adsorbent for the removal of malachite green from aqueous solution. Experimental data provided best fit with Langmuir equation, indicating monolayer sorption on a homogeneous surface. Monolayer sorption capacity which increased with the increasing of temperature in the range 288–308 K for malachite green sorption was obtained to be 29.4 mg g^{-1} at 308 K. Sorption of malachite green on *L. cylindrica* seems to be favorable process. The kinetic study demonstrates that sorption process follows pseudo-second-order kinetic model. The lowest half-sorption time was obtained at 308 K in the studied temperature range. From thermodynamic study spontaneous and endothermic nature of sorption were observed. When pH of the solution increased from 3 to 5, the amount of adsorbed malachite green also rose up. Beyond pH 5, the amount of adsorbed malachite green remained constant. In other words, malachite green sorption from aqueous solution onto AL was unfavorable at $\text{pH} < 5$.

References

- [1] N.M. Mamdouh, M.S. El-Geundi, Comparative cost of color removal from textile effluents using natural adsorbents, *J. Chem. Technol. Biotechnol.* 50 (1991) 257–264.
- [2] L.C. Morais, O.M. Freitas, E.P. Gonçalves, L.T. Vascancelos, C.G. González Beça, Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process, *Water Res.* 33 (1999) 979–988.
- [3] M.-S. Chiou, H.-Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads, *J. Hazard. Mater.* 93 (2002) 233–248.
- [4] V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, Adsorption of basic dyes on granular activated carbon and natural zeolite, *Water Res.* 35 (2001) 3357–3366.
- [5] A. Sari, M. Tuzen, Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies, *J. Hazard. Mater.* 157 (2008) 448–454.
- [6] R.A. Anayurt, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass, *Chem. Eng. J.* 151 (2009) 255–261.
- [7] A. Sari, M. Tuzen, Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (*Ulva lactuca*) biomass, *J. Hazard. Mater.* 152 (2008) 302–308.
- [8] A. Sari, M. Tuzen, Ö.D. Uluözülü, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass, *Biochem. Eng. J.* 37 (2007) 151–158.
- [9] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. basic green 4 (malachite green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, *Sep. Purif. Technol.* 53 (2007) 97–110.
- [10] Y. Onal, C. Akmil-Basar, C. Sarici-Ozdemir, Investigation kinetics mechanisms of adsorption malachite green onto activated carbon, *J. Hazard. Mater.* 146 (2007) 194–203.
- [11] I.A. Rahman, B. Saad, S. Shaidan, E.S. Sya Rizal, Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical–thermal process, *Bioresour. Technol.* 96 (2005) 1578–1583.
- [12] S. Rajgopal, T. Karthikeyan, B.G. Prakash Kumar, L.R. Miranda, Utilization of fluidized bed reactor for the production of adsorbents in removal of malachite green, *Chem. Eng. J.* 116 (2006) 211–217.
- [13] V.K. Garg, R. Kumar, R. Gupta, Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*, *Dyes Pigments* 62 (2004) 1–10.
- [14] A. Mittal, Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers, *J. Hazard. Mater.* B133 (2006) 196–202.
- [15] R. Gong, Y. Jin, F. Chen, J. Chen, Z. Liu, Enhanced malachite green removal from aqueous solution by citric acid modified rice straw, *J. Hazard. Mater.* 137 (2006) 865–870.
- [16] K.V. Kumar, S. Sivanesan, Pseudo second order kinetics and pseudo isotherms for malachite green onto activated carbon: comparison of linear and non-linear regression methods, *J. Hazard. Mater. B* 136 (2006) 721–726.
- [17] S.-C. Chang, M.-S. Lee, C.-H. Li, M.-L. Chen, Dietary fibre content and composition of vegetables in Taiwan area, *Asia Pacific J. Clin. Nutr.* 4 (1995) 204–210.
- [18] B.N. Sastri, Wealth of India: a dictionary of Indian raw materials and industrial products, *CSIR Res.* 6 (1962) 179.
- [19] T. Pekdemir, B. Keskinler, E. Yildiz, G. Akay, *J. Chem. Technol. Biotechnol.* 78 (2003) 773–780.
- [20] J.P. Chen, S.C. Yu, B.R. Hsu, S.H. Fu, H.S. Liu, Loofa sponge as a scaffold for the culture of human hepatocyte cell line, *Biotechnol. Prog.* 19 (2003) 522–527.
- [21] C.A. Boynard, S.N. Monteiro, J.R.M. d'Almeida, Aspects of alkali treatment of sponge gourd (*Luffa cylindrica*) fibers on the flexural properties of polyester matrix composites, *J. Appl. Polym. Sci.* 87 (2003) 1927–1932.
- [22] S. Lagergren, About the theory of so-called adsorption of soluble substances, *K. Sven. Vetenskapsakad. Handl.* 24 (4) (1898) 1–39.
- [23] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1978) 115–124.
- [24] M. Doğan, H. Abak, M. Alkan, Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters, *J. Hazard. Mater.* 164 (2009) 172–181.
- [25] E. Bulut, M. Ozacar, I.A. Sengil, Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design, *Microporous Mesoporous Mater.* 115 (2008) 234–246.
- [26] C. Gérente, V.K.C. Lee, P. Le Cloirec, G. McKay, Application of chitosan for the removal of metals from wastewaters by adsorption—mechanisms and models review, *Crit. Rev. Env. Sci. Technol.* 37 (2007) 41–127.
- [27] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (malachite green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, *Sep. Purif. Technol.* 53 (2007) 97–110.
- [28] B.H. Hameeda, M.I. El-Khaiaryb, Malachite green adsorption by rattan sawdust: isotherm, kinetic and mechanism modeling, *J. Hazard. Mater.* 159 (2008) 574–579.
- [29] V.K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash, *Sep. Purif. Technol.* 40 (2004) 87–96.
- [30] D. Ghosh, G.K. Bhattacharyya, Adsorption of methylene blue on kaolinite, *Appl. Clay Sci.* 20 (2002) 295–300.
- [31] G.K. Bhattacharyya, A. Sarma, Adsorption characteristics of the dye, brilliant green on neem leaf powder, *Dyes Pigments* 57 (2003) 211–222.
- [32] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57 (1906) 385–470.
- [33] M.M. Dubinin, L.V. Radushkevich, Equation of the characteristic curve of activated charcoal, *Proc. Acad. Sci. U.S.S.R.* 55 (1947) 331–333.
- [34] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, second ed., Academic Press, London, UK, 1982.
- [35] S.M. Hasany, M.H. Chaudhary, Sorption potential of Haro river sand for the removal of antimony from acidic aqueous solution, *Appl. Radiat. Isot.* 47 (1996) 467–471.

- [36] A. Benhammoua, A. Yaacoubi, L. Nibou, B. Tanouti, Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies, *J. Colloid Interface Sci.* 282 (2005) 320–326.
- [37] J.P. Hobson, Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure, *J. Phys. Chem.* 73 (1969) 2720–2727.
- [38] S.S. Tahir, N. Rauf, Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay, *Chemosphere* 63 (2006) 1842–1848.
- [39] J. Zhang, Y. Li, C. Zhang, Y. Jing, Adsorption of malachite green from aqueous solution onto carbon prepared from *Arundo donax* root, *J. Hazard. Mater.* 150 (2008) 774–782.
- [40] M.J. Iqbal, M.N. Ashiq, Adsorption of dyes from aqueous solutions on activated charcoal, *J. Hazard. Mater.* B139 (2007) 57–66.
- [41] Z. Bekci, Y. Seki, L. Cavas, Removal of malachite green by using an invasive marine alga *Caulerpa racemosa* var. *Cylindracea*, *J. Hazard. Mater.* 161 (2009) 1454–1460.